Chemiluminescent Reaction Processes Pertinent to
the Chemosphere in the Micron Pressure Region

by

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ABSTRACT

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Some atom reactions which result in light emission have been studied in a vacuum system operating in the 5 to 30 micron pressure region. At these low pressures two body reaction processes may dominate in certain cases as was shown previously for the nitric oxide-oxygen atom reaction and the sulfur monoxide-oxygen atom reaction.

The visible chemiluminescent recombination reaction of nitrogen atoms at low pressures approaches second order which can be attributed to an inverse predissociation process. A tentative mechanism can be given as:

$$N + N \rightleftarrows N_2 \quad {}^5\Sigma_g^+ \rightleftharpoons N_2 \; B\,{}^3\Pi_g \rightarrow N_2 A \; {}^3\Sigma_u^+ + h\nu,$$
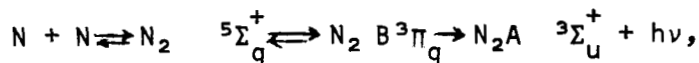
where the rate for the light emission is estimated as $k = 10^{-19\pm1}$ $(cm^3/particles)\ sec^{-1}$

Introduction

In general chemiluminescent reactions in the upper atmosphere can be divided into two groups; those occurring between ambient reactants and those due to addition of a reactant into the atmosphere by release from a rocket. A large number of different reactions are therefore of interest, but in almost all atoms are involved.

Four types of reactions which may occur to produce light emission pertinent to the upper atmosphere are:

First, a general exothermic two body reaction such as

$$O_3 + H \rightarrow O_2 + OH^{\ddagger} \qquad (1)$$
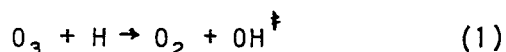
where the $OH^{\ddagger}$ emits the well known Meinel bands.[1]

A second type is due to the direct three body recombination as frequently occurs in atom recombination such as the emission of NO beta bands in the N plus O atom recombination.[2]

A third, is a direct two body recombination as with NO and oxygen atoms with the emission of a continuum:[3,4]

$$NO + O \rightarrow NO_2 + h\nu$$
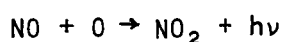
A fourth possibility is the similar two body recombination by an inverse predissociation process.

The reactions of nitric oxide with oxygen atoms,[3] and sulfur monoxide with oxygen atoms[5] have been previously studied in our low pressure reaction vessel. The purpose of

the present work was to extend this work to study the after-

glow and recombination process of nitrogen atoms.

Experimental

The low pressure system previously reported has now

been used for the study of the chemiluminescent emission due

to nitrogen atoms, i.e. the Lewis Rayleigh afterglow; see

Figure 1. For this purpose several minor modifications were

necessary. In this case a condensed D.C. discharge was used

to produce relatively high concentrations of nitrogen atoms

(3 to 5%). The pressure was measured by use of a diaphram

gauge (Differential pressure meter, Model 306-Decker Corp.)

where the response is independent of the nature of the gas.

The alphatron gauges previously used were not stable when a

condensed discharge was running, whereas the DPM was unaffec-

ted by electrical noise.

Results

The relative light intensity of the Lewis-Rayleigh

afterglow was measured versus pressure in analogous fashion

to the previous work.[3,5] This afterglow intensity increased

with pressure by $p^{2.50\pm0.10}$ in the pressure range of 5 to 30

microns. See Table I. The slope or exponent is equivalent to

the effective order of the reaction and was generally higher

when measured in a higher pressure region - 10 to 27 microns.

The addition of helium or argon was made to vary

the effect of the third body as is well known for the Lewis-

Rayleigh afterglow, and it was noted that the afterglow inten-
sity was now very close to second order in the whole 8 to 27
micron region- See Table I. In addition the change of inten-
sity was measured when the gas was expanded from 200 to 10μ
and the analogous results had been obtained.

It should be noted that the observed emission in the
visible region is indicative of only a part of the overall re-
combination and is therefore no direct measure of the total
rate and overall order for the recombination of nitrogen atoms.

No effect of light emission due to wall catalysis
was anticipated or observed as was reported with oxygen atoms.[6]

Discussions

Despite many studies in the field of active nitrogen
there are fundamental problems which still exist. One question
involves the problem of nitrogen atom concentration versus the
concentration of metastable molecules and reactive species de-
pending on the method of generation of the active nitrogen and
the means used to determine these concentrations.

The mechanism of the recombination appears to be
quite complex involving an initial formation of $^5\Sigma_g^+$, $^3\Sigma_u^+$,
and/or $^1\Sigma_g^+$ states as required by the correlation rules of
Wigner-Witmer. A general mechanism has been given in some de-
tail which can explain many of the observations.[8,9] The chemi-
luminescence recombination is apparently only a fraction of the
total recombination. The measured overall rate coefficient is

3×10^{-32} $(cm^3/particle)^2$ sec^{-1}; the rate for chemiluminescent recombination emission may be only a fraction of this, or about 10^{-33} $(cm^3/particle)^2$ sec^{-1}.[10]

The usual mechanism considered for nitrogen atom re-combinations results in a third order dependency for the light emission as well as for N-atom consumption.

In the present work precise measurements were made of the order of the light emitting reaction in the 5 to 30 micron pressure region. The order observed was definitely less than three (average 2.50) and with mixtures containing more than 90% argon or helium, was around two. A reaction order between 2 and 3 could be interpreted to mean that competing second and third order processes are occurring. Argon or helium are less efficient as third bodies and would result in reducing the third order contribution. The results with argon and helium, therefore, lend support to the interpretation of competing second and third order reactions, where the second order reaction can now dominate.
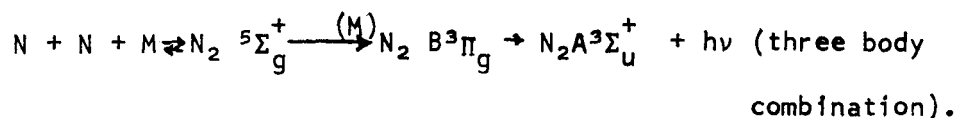
Several processes may be considered to account for a second order dependence of the light emission. If the emission at low pressures appeared as a continuum, a direct recombination of atoms would appear likely. Alternately if the spectral character of the emission does not change drastically, it would seem most probable that an inverse predissociation mechanism is occurring.

The light emission in the micron pressure is very weak, and therefore high resolution spectroscopic measurements are difficult to obtain. Low resolution spectra were obtained by using a large slit, with a transmission grating attached to a 35 mm camera. From these spectra it appeared as if the type of emission at low pressures, about 10μ, was approximately the same as at high pressure, 300μ; a distinction between bands with sharp lines and diffuse band emission obviously was impossible. By using transmission filters in front of the photomultiplier, it was possible to measure relative intensities over various portions of the spectrum of the afterglow. The ratio of intensities changed between experiments at higher and lower pressures, and this may be indicative in this case of some changes in the character of the afterglow emission. Changes observed in this manner are substantial. See Table II

Since a second order dependency is obtained for the light emission and the emission is not a continuum, it may be reasonable to conclude that some inverse predissociation process is operative, such as:

$$N + N \rightleftharpoons N_2 \; {}^5\Sigma_g^+ \rightleftharpoons N_2 \; B^3\Pi_g \rightarrow N_2 A^3\Sigma_u^+ + h\nu \text{ (inverse predis-}$$

$$\text{sociation)}$$
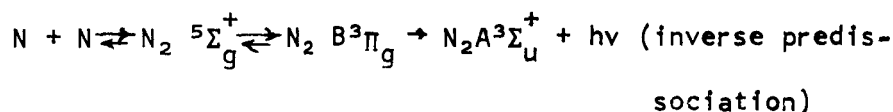
compared to the generally accepted three body process:

$$N + N + M \rightleftharpoons N_2 \; {}^5\Sigma_g^+ \xrightarrow{(M)} N_2 \; B^3\Pi_g \rightarrow N_2 A^3\Sigma_u^+ + h\nu \text{ (three body}$$

$$\text{combination).}$$

Under these conditions the emission spectrum should be diffuse having a maxima in those regions where the band

heads had been observed. It is likely that the ratio of these intensities will not be the same as when the N_2 ${}^5\Sigma_g^+$ and/or N_2 $B^3\pi_g$ were stabilized by collisions.

The rate of the two body inverse predissociation process was estimated as $10^{-19\pm1}$ $(cm^3/particle)$ sec^{-1}. This is 100 to 1000 times slower than the rate of the reaction $NO + O \rightarrow NO_2 + h\nu$.

In connection with the upper atmosphere, however, the net consumption of N-atoms would still be due to reactions over molecular oxygen. The rate for this reaction ($N + O_2 \rightarrow NO + O$) is about 10^{-16} $(cm^3/particle)$ sec^{-1} with 6 kilocalories heat of activation with increasing temperatures above 100 kilometers altitude the rate would increase and N-atoms will react much more readily with the molecular oxygen, than in a two body recombination process with another N-atom.

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TABLE I

Equivalent order of reaction, n, as measured by
relative emission intensity with increasing
pressure ($I \sim p^n$)

Pressure region	Observed reaction order, n	
100% N_2		
5 to 12μ	2.49	
9 to 18μ	2.56	Average = 2.50 $\pm$ 0.10
10 to 27μ	2.60	
5% N_2 balance Argon		
12 to 18μ	1.90	Average = 1.90 $\pm$ 0.10
10% N_2 balance Helium		
9 to 18μ	2.15	
8 to 27μ	1.93	Average = 2.05 $\pm$ 0.10
12 to 27μ	2.07	

Atom concentrations were maintained relatively constant between
3 and 5%

TABLE II
Observation of Relative Intensities of
the Nitrogen Afterglow

Corning Filter	3-68	3-66	2-61	
For 100% N_2	1.0	0.53_7	0.30_8	200μ Pressure
	1.0	0.44_6	0.25_9	10μ Pressure
For 5% N_2	1.0	0.52_0	0.30_7	200μ Pressure
Balance Argon	1.0	0.41_8	0.25_2	10μ Pressure

Corning Filter 3-68 Transmits the red yellow and green

3-66 Transmits the red and yellow

2-61 Transmits the red

Measurements were made only in the visible region of the spectrum

MECHANICAL PUMP

MECHANICAL PUMP

MERCURY PUMP

DIAPHRAM PRESSURE GAUGE

REACTION TUBE

PHOTO MULTIPLIER

B

NO

50 LITER VESSEL

6" LIQUID NITROGEN TRAP

A

PHOTO MULTIPLIER
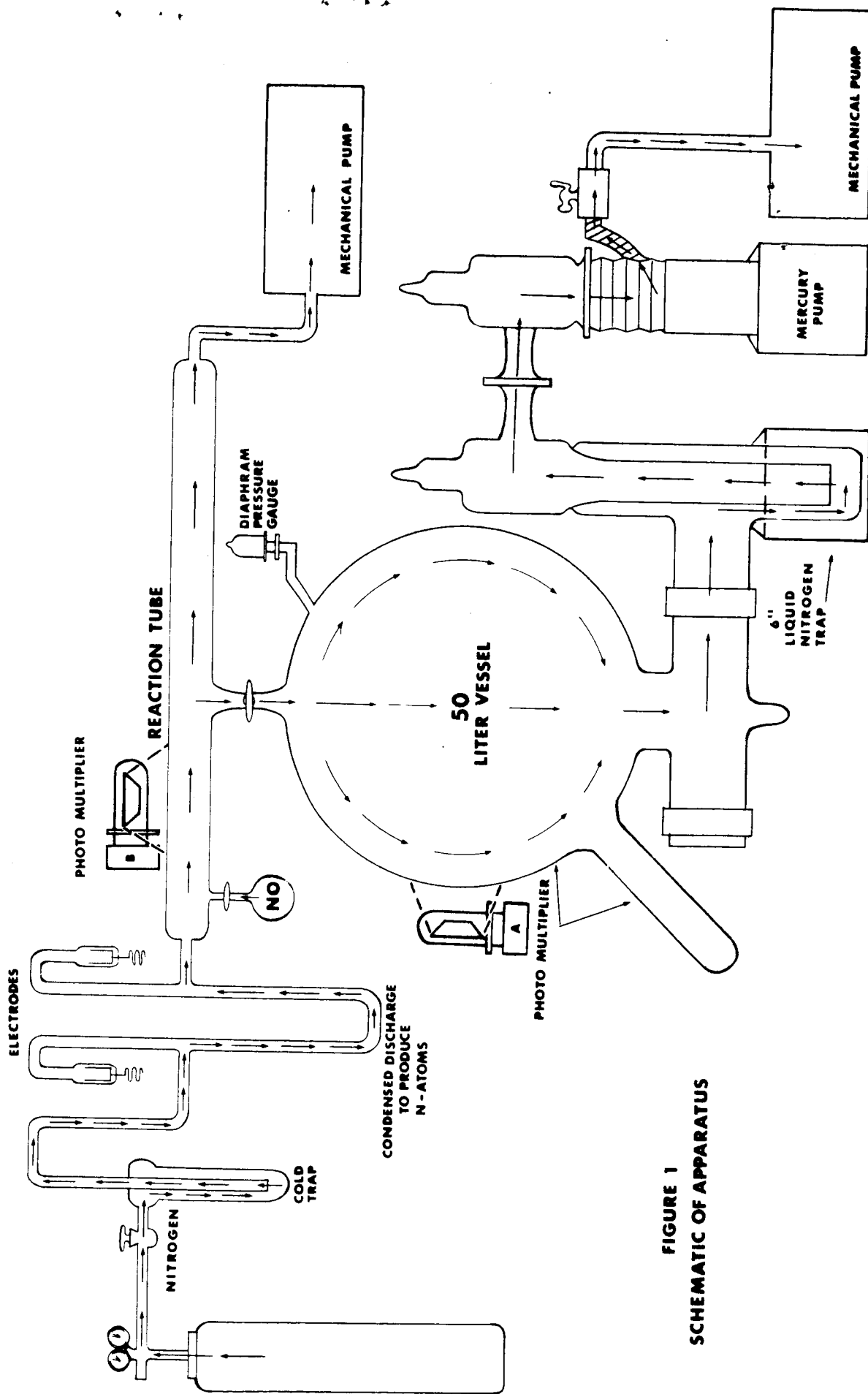
ELECTRODES

CONDENSED DISCHARGE TO PRODUCE N-ATOMS

COLD TRAP

NITROGEN

FIGURE 1

SCHEMATIC OF APPARATUS